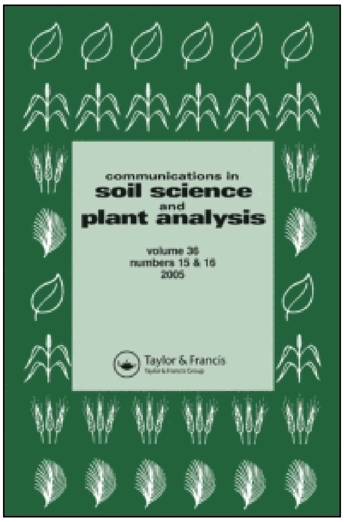

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Assessment of Mehlich3 and Ammonium Bicarbonate-DTPA Extraction for Simultaneous Measurement of Fifteen Elements in Soils

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Assessment of Mehlich3 and Ammonium Bicarbonate-DTPA Extraction for Simultaneous Measurement of Fifteen Elements in Soils

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ABSTRACT

Few existing extractions such as Mehlich3 and ammonium bicarbonate-DTPA (ABDTPA) can be used as a multi-element soil test. A multi-element extraction is attractive to scientists and soil testing laboratories because it eliminates the need for multiple extractions and allows simultaneous measurement of elements by using the Inductively Coupled Plasma (ICP). The objective of this study was to evaluate Mehlich3 and ABDTPA for simultaneous measurement of 15 elements in 30 acidic and 20 alkaline U.S. soils from 21 states. Widely-accepted, and conventional soil tests (Bray1 and Olsen for phosphorus (P); NH_4OAc for calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na); diluted HCl

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and DTPA for aluminum (Al), cadmium (Cd), cobalt (Co), chromium (Cr), Copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn) were employed for the evaluation. Single and multiple regression analysis were applied to investigate the relationship between Mehlich3 or ABDTPA and the respective soil test. The results can be summarized: 1) Mehlich3 provided a good measurement for labile P in all soils while ABDTPA provided reliable results for alkaline soils; 2) Mehlich3 was a suitable extract for Ca, Mg, K, and Na for all soils while ABDTPA could not be used for Ca; 3) Mehlich3 or ABDTPA was an appropriate extract for Al, Cd, Cu, Fe, Mn, Ni, Pb, and Zn in all soils. The fact that most soils investigated had trace amounts of Co, and Cr hindered their evaluation. Accordingly, Mehlich3 extraction could be recommended for simultaneous measurement of at least 13 elements in soils.

Key Words: Multi-element soil test; Available phosphorus; Soluble heavy metals; Exchangeable cations.

INTRODUCTION

In 1984, Mehlich modified his original soil extract to develop Mehlich3 solution,[1] which is suitable to extract P and other elements. The Mehlich3 solution is a combination of acids (0.2 *M* HOAc and 0.013 *M* HNO_3), ammonium salts (0.015 *M* NH_4F and 0.25 *M* NH_4NO_3), and 0.001 *M* of the chelating agent ethylenediaminetetraacetic acid (EDTA). Hydrogen, F^-, and OAc^- are the principle ions used in Mehlich3 solution to remove P from soils. Exchangeable cations (i.e., Ca, Mg, K, and Na) are extracted mainly by the action of H^+, and NH_4^+ ions. Metals (i.e., Fe, Mn, Cu, and Zn) are extracted by H^+, and NH_4^+ ions, and the chelating agent EDTA.

The ammonium bicarbonate-diethylenetriaminepentaacetic acid (ABDTPA) solution was developed by Soltanpour and Schwab[2] to simultaneously extract labile P, K, Fe, Mn, and Cu from neutral and alkaline soils. The ABDTPA solution is 1.0 *M* NH_4HCO_3 and 0.005 *M* DTPA, adjusted at pH 7.6. It removes soil P with HCO_3^-, and NH_4^+ is used for the extraction of K, and DTPA is applied for the chelation of metals (Fe, Mn, Cu, and Zn).

Both Mehlich3-, and ABDTPA-extractable elements were found to be closely related to those determined by existing soil tests.[3,4] Using a multielement extraction method is attractive to soil testing laboratories because 1) it eliminates the need for multiple extractions for P, exchangeable bases, and heavy metals; and 2) it allows for simultaneous measurement of all elements by the Inductively Coupled Plasma Spectroscopy (ICP).

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The objective of this study was to evaluate both Mehlich3 and ABDTPA extraction methods for the simultaneous extraction and measurement of 15 elements (P, Ca, Mg, K, Na, Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in soils. We used widely accepted and conventional soil tests to evaluate the two extraction methods. These soil tests included Bray1[5] and Olsen[6] for available P; neutral 1.0 *M* NH4OAc for exchangeable cations; 0.1 *M* HCl,[7] and DTPA[8] for metals. Our study covered several elements (i.e., Al, Cd, Ni, and Pb) that were not included in the original Mehlich3 and ABDTPA methods.

MATERIALS AND METHODS

A total of 50 surface samples were selected from 40 benchmark soils of the United States. The soils (collected in 21 different states) varied greatly in their physical and chemical properties and included 30 acidic and 20 alkaline and calcareous soils (Table 1). Two or more samples were collected from some benchmark soils. For these soils, numbers in parenthesis next to the soil name represents the sample number.

Soil analysis were performed by methods described in the Soil Survey Investigations Report (SSIR) No. 42.[9] Alphanumeric codes in parentheses next to each method indicate specific standard operating procedures. Analysis was conducted on air-dried < 2-mm soil samples. Particle-size analysis was performed by sieve and pipette method (3A1). Total carbon content was determined by dry combustion (6A2f), and $CaCO_3$ equivalent was estimated by the manometer method (6E1g). Organic carbon (OC) was calculated from the difference between total and inorganic carbon in soil. Soil pH was measured in a 1:1 soil/water paste (8C1f). Exchangeable Ca, Mg, K, and Na were determined by the neutral 1.0 *M* NH_4OAc method (5A8c). Classification and properties for soils are given in Table 1.

The Mehlich3,[1] ABDTPA,[2] DTPA,[8] and the 0.1 *M* HCl[7] soil extracts were prepared as described in the respective references. The available soil P was extracted according to Bray and Kurtz[5] and Olsen et al.,[6] respectively.

Phosphorus, exchangeable cations (Ca, Mg, K, and Na), and metals (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) were measured in the soil extracts with the Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), (Perkin Elmer 3300 DV).

To evaluate Mehlich3 and ABDTPA extraction methods, the 15 elements were investigated under three categories: phosphorus, exchangeable cations (Ca, Mg, K, and Na), and metals (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn). For each category, conventional soil tests were selected to

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Table 1. Classification and properties for 30 acidic and 20 alkaline & calcareous soils investigated.

Serial #	Soil	Classification	Clay (%)	CaCO3 (%)	OC (g/Kg)	pH
Acidic soils						
1	Nevine	Loamy-skeletal, Mixed, Superactive frigid typic vitrixerand	5.00	ud	33.08	6.40
2	Stecum	Sandy-skeletal, Mixed lithic cryumbrept	1.30	ud	8.33	5.70
3	Bojac (1)	Coarse-loamy, Mixed, Thermic typic hapludult	15.00	ud	14.21	5.30
4	Selle	Sandy, Mixed, Frigid vitrandic dystrochrept	4.10	ud	35.92	5.60
5	Rubson	Coarse-silty, Mixed, Superactive vitrandic glossoboralf	5.80	ud	11.37	6.50
6	Porthill	Fine, Mixed, Superactive typic eutroboralf	9.50	ud	69.00	5.70
7	Wickham (1)	Fine-loamy, Mixed, Thermic typic hapludult	8.80	ud	5.62	5.50
8	Wickham (2)	Fine-loamy, Mixed, Thermic typic hapludult	9.10	ud	6.87	5.10
9	Bojac (2)	Coarse-loamy, Mixed, Thermic typic hapludult	7.80	ud	7.67	4.80
10	Valusia	Fine-loamy, Mixed, Mesic aeric fragiaquept	9.80	ud	54.16	4.40
11	Balta	Fine, Smectitic, Mesic typic haplustalf	35.10	ud	12.37	6.70
12	Denham	Sandy, Mixed, Mesic oxyaquic udipsamment	3.10	ud	2.96	6.30
13	Dickson	Fine-silty, Siliceus, Semiactive, Mesic glossic fragiudult	10.50	ud	11.52	6.30
14	Woodburn	Fine-silty, Mixed, Mesic aquultic argixeroll	17.00	ud	25.49	5.90
15	Albia (1)	Fine-loamy, Mixed, Mesic aeric fragiaqualf	16.30	ud	13.34	6.00
16	Albia (2)	Fine-loamy, Mixed, Mesic aeric fragiaqualf	18.10	ud	80.82	5.30
17	Moon	Loamy, Mixed, Active, Nonacid, Mesic oxyaquic hapludalf	3.40	ud	11.96	6.40
18	Tujunga	Sandy, Mixed, Isotic, Frigid dystric xeropsamment	4.90	ud	48.14	6.20
19	Murrill	Fine-loamy, Mixed, Mesic typic hapludult	18.50	ud	15.83	6.40
20	Penwood	Sandy, Mixed, Mesic typic udipsamment	3.40	ud	6.24	5.40
21	Tunica	Clayey over loamy, Smectitic, Thermic vertic haplaquept	29.70	ud	14.39	6.10
22	Tunica	Clayey over loamy, Smectitic, Thermic vertic haplaquept	30.80	ud	8.54	6.20
23	Patapsco	Loamy, Siliceous, Mesic grossarenic kandiudult	1.20	ud	4.00	5.00
24	Wist	Fine-loamy, Mixed, Active, Mesic typic hapludult	8.80	ud	19.76	5.50

25	Ormas	Loamy, Mixed, Mesic arenic hapludalf	1.30	ud	6.65	5.80
26	Boyer	Coarse-loamy, Mixed, Mesic typic hapludalf	4.20	ud	11.61	4.60
27	Pootatuck	Coarse-loamy, Mixed, Active, Mesic fluvaquentic dystrudept	5.70	ud	31.19	6.70
28	Crisfield	Coarse-loamy, Mixed, Thermic udic haplustoll	6.10	ud	2.15	5.00
29	Capac	Fine-loamy, Mixed, Active, Mesic aquic glossudalf	24.20	ud	29.86	6.90
30	Allard	Coarse-silty, Mixed, Active, Mesic typic dystrudept	16.90	ud	19.88	6.10
Alkaline & calcareous soils						
1	Windthorst	Fine, Mixed, Thermic udic paleustalf	18.70	9.00	54.17	7.40
2	Maloterre	Loamy-skeletal, Carbonatic, Thermic lithic ustochrept	29.30	35.00	75.77	7.80
3	Frisite	Fine-loamy, Mixed, Active, Mesic typic calciargid	19.60	6.00	22.31	8.20
4	Eastall	Fine, Smectitic, Thermic ustic epiaquert	55.30	1.00	15.12	8.00
5	Vinson	Coarse-loamy, Mixed, Superactive, Thermic oxyaquic haplustoll	14.50	ud	7.98	7.70
6	McCarthy	Sandy-skeletal, Isotic, Mesic typic vitrandept	3.90	ud	35.57	7.40
7	Limon	Fine-silty, Mixed, Superactive, Mesic eutic haplustert	46.00	1.00	17.61	7.90
8	Heldt (1)	Fine, Smectitic, Mesic, Torrertic haplustalf	46.60	2.00	21.95	7.80
9	Heldt (2)	Fine, Smectitic, Mesic, torrertic haplustalf	46.50	1.00	19.31	7.60
10	Broseley	Loamy, Mixed, Thermic arenic hapludalf	42.20	2.00	16.04	7.90
11	Goshen	Fine-loamy, Mixed, Mesic pachic argiustoll	25.90	ud	12.77	7.00
12	Deale	Fine-silty, Mixed, Active, Mesic aeric endoaquult	16.60	ud	13.41	7.20
13	Greenson (2)	Fine-silty, Mixed, Superactive, Mesic oxyaquic calcixeroll	20.90	2.00	20.86	7.80
14	Greenson (1)	Fine-silty, Mixed, Superactive, Mesic oxyaquic calcixeroll	19.20	3.00	34.76	7.40
15	Greenson (3)	Fine-silty, Mixed, Superactive, Mesic oxyaquic calcixeroll	31.20	1.00	18.35	7.70
16	Layton	Sandy, Mixed, Superactive, Mesic, Oxyaquic haploxeroll	4.20	1.00	12.66	8.80
17	Coly (1)	Fine-silty, Mixed calcareous, Mesic typic ustorthent	23.50	3.00	16.83	8.10
18	Coly (2)	Fine-silty, Mixed calcareous, Mesic typic ustorthent	23.60	2.00	15.81	7.70
19	Coly (3)	Fine-silty, Mixed calcareous, Mesic typic ustorthent	26.80	0.10	16.10	7.90
20	Coly (4)	Fine-silty, Mixed calcareous, Mesic typic ustorthent	27.70	0.10	14.13	7.30

ud = undetected; OC = organic carbon.

evaluate the two extraction methods. Throughout this report, we referred to the Mehlich3 and ABDTPA as extraction methods while conventional extractions used for the evaluation were referred to as tests.

For P, the Bray1 test[5] was used to evaluate both Mehlich3 and ABDTPA extraction methods in acidic soils while Olsen test[6] was applied for the evaluation in alkaline and calcareous soils. For cations (Ca, Mg, K, and Na), the neutral 1.0 *M* NH_4OAc test was used for the evaluation in both acidic and alkaline soils. For metals (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn), the 0.1 *M* HCl,[7] and DTPA test[8] were employed for the evaluation of the two extraction methods in acidic and alkaline soils, respectively.

Stepwise multiple regression models of SAS version 8.2[10] were employed for the statistical analysis.

RESULTS AND DISCUSSIONS

Phosphorus

The average and range of P removed by Mehlich3, and ABDTPA extraction methods, and Bray1, and Olsen tests for all soils investigated are given in Table 2. For acidic soils, Mehlich3-P ranged between 18.7 and 281.8 mg/Kg soil with an average of 114.9 mg/Kg soil. The Mehlich3-P data in general were similar to those obtained by Bray1 test. Fluoride, in an acidic soil environment, can complex Al and Fe ions associated with Fe- and Al-phosphates, which releases P into solution.[11] Hydrogen and F^- are the principle ions used by both Mehlich3 and Bray1 to dissolve P minerals in soils, which may explain the similar amounts of P removed.

Table 2. Average and range of P removed by Mehlich3 and ABDTPA extraction methods, and Bray1 and Olsen test (mg/Kg soil) for 30 acidic, and 20 alkaline soils investigated.

Soils		Mehlich3	Bray1	ABDTPA	Olsen
		(mg P/Kg soil)			
Acidic	Average	114.91	121.52	27.98	32.04
	Min	18.65	1.85	5.95	4.92
	Max	281.75	548.8	94.19	89
Alkaline	Average	207.48	117.76	61.29	98.57
	Min	54.55	39.55	10.74	16.35
	Max	585.25	276.2	240.35	475

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Phosphorus removed from acidic soils by ABDTPA method was lower than that removed by Mehlich3 and Bray1 and ranged from 5.95 to 94.2 mg/Kg soil with an average of 28.0 mg/Kg soil. Both ABDTPA method and Olsen test removes soil P with HCO_3^- ions and mainly from Ca-phosphates.[12] Acidic soils contain predominately Al-, and Fe-phosphates.[13] Moreover, H^+ and F^- ions are more effective in dissolving P minerals than bicarbonate ions.[14] This difference may explain the lower amounts of P removed by ABDTPA when compared with both Mehlich3 and Bray1.

For acidic soils, a highly significant correlation was obtained between Mehlich3-P or ABDTPA-P and that P extracted with Bray1 test (Figure 1-a,b). However, the relationship with Mehlich3 (r = 0.863**) appeared to be stronger than that with ABDTPA (r = 0.503**). This indicated that Mehlich3

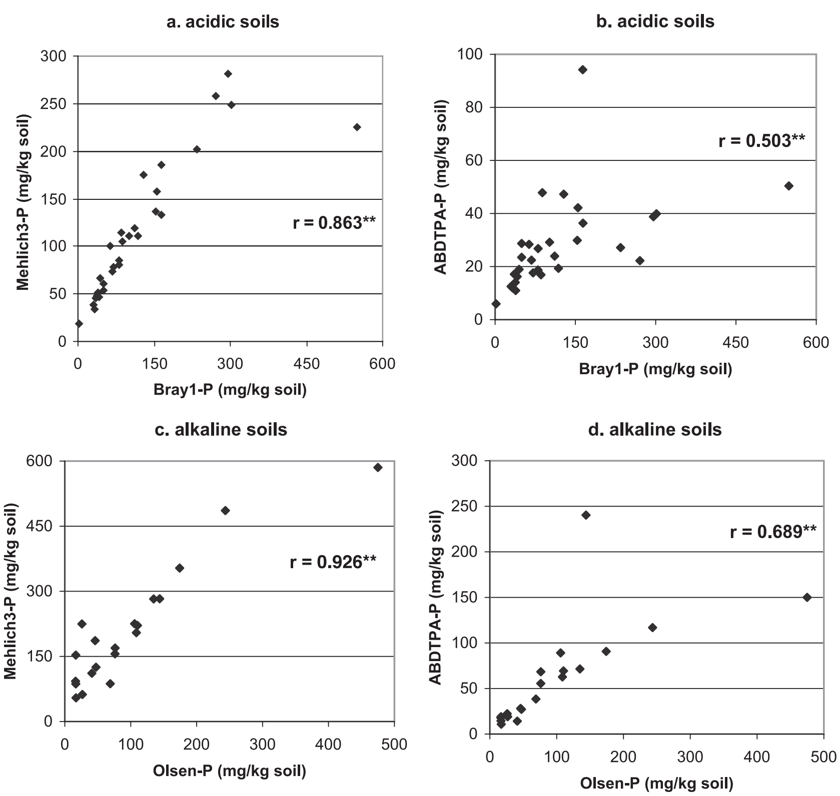

Figure 1. Relationship between Mehlich3- or ABDTPA-, and Bray1-extractable P for 30 acidic soils (a, b), and Olsen-extractable P for 20 alkaline soils (c, d).

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was a relatively better P index than ABDTPA for acidic soils investigated. A similar relationship was obtained for 44 acidic soils in Florida where Elrashidi et al.[14] found highly significant correlation between Bray1-P and Mehlich3-P (r = 0.983**) or ABDTPA-P (0.686**). Hanlon and Johnson[15] also reported a good correlation between ABDTPA-P and Bray1-P for acidic soils in Oklahoma.

Incorporation of soil properties with Mehlich3-P or ABDTPA-P in a multiple regression model might improve the relationship with P soil test (Bray1 or Olsen). Applying SAS Stepwise program,[10] we included properties known to influence P solubility in soils (i.e., pH, $CaCO_3$, clay, and OC) along with Mehlich3-P or ABDTPA-P to determine the best two-variable regression models (Table 3).

For acidic soils, we found that including pH with Mehlich3-P or ABDTPA-P gave the best two-variable models. The best model of Mehlich3-P and ABDTPA-P could account for 79.4 and 27% of variations in the value of Bray1-P, respectively. These data confirmed the reliability of Mehlich3 extraction method for acidic soils investigated. It also implied that ABDTPA method was not as good of a P extraction as Mehlich3 for acidic soils.

For alkaline soils, Mehlich3 removed higher amounts of P than ABDTPA and Olsen (Table 2). The average of Mehlich3-P extracted was 207 mg/Kg soil while that of ABDTPA-P and Olsen-P was 61.3 and 98.6 mg/Kg soil, respectively. As mentioned above, Mehlich3 uses more aggressive mechanisms than both ABDTPA and Olsen to dissolve P minerals in soils.

Table 3. Best two-variable regression models relating Mehlich3 or ABDTPA extraction method and soil properties to Bray1 and Olsen test for 30 acidic, and 20 alkaline soils investigated.

Soils	Independent variable	Best two-variable model	R2
Acidic	Bray1-P	Bray1-P = 189.8 + 1.34(Mehlich3-P) − 38.4(pH)	0.794**
		Bray1-P = 171.9 + 3.09(ABDTPA-P) − 23.6(pH)	0.270**
Alkaline	Olsen-P	Olsen-P = − 25.2 + 0.51(Mehlich3-P) + 5.49(CaCO3)	0.937**
		Olsen-P = 16.3 + 0.80(ABDTPA-P) + 9.52(CaCO3)	0.875**

**Indicates 1% significant level of correlation.

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Both Mehlich3-P and ABDTPA-P methods showed highly significant correlation with Olsen-P test for alkaline soils investigated (Figure 1-c,1d). Unexpectedly, Mehlich3-P gave relatively stronger relationship with Olsen-P ($r = 0.926^{**}$) than that obtained with ABDTPA-P ($r = 0.689^{**}$). Burt et al.,[16] in their study on 21 benchmark soils of the U.S., reported similar correlation ($r = 0.933^{**}$) between Mehlich3-P and Olsen-P.

In multiple regression analysis, we found that including $CaCO_3$ with Mehlich3-P or ABDTPA-P produced the best two-variable models that can predict Olsen-P for alkaline soils (Table 3). A model included $CaCO_3$ with Mehlich3-P or ABDTPA-P could predict 93.7 and 87.5% of variations in the value of Olsen-P, respectively. These data indicated that either Mehlich3 or ABDTPA can be considered a suitable P extraction for alkaline soils investigated.

Table 4. Average and range of Ca, Mg, K, and Na extracted by Mehlich3 and ABDTPA extraction methods, and NH4OAc test (mg/kg soil) for 30 acidic, and 20 alkaline soils investigated.

		Ca	Mg	K	Na
Soils		(mg/kg soil)			
Mehlich3-extractable cations					
Acidic	Average	1230.9	210.9	182.8	31.4
	Min	234.0	8.5	15.3	11.7
	Max	3349.0	848.6	520.4	85.5
Alkaline	Average	5242.8	813.7	828.4	119.9
	Min	2393.0	53.0	38.0	24.8
	Max	10949.0	1573.0	1715.0	447.3
ABDTPA-extractable cations					
Acidic	Average	321.8	126.6	156.2	15.1
	Min	73.6	3.5	21.3	4.8
	Max	576.2	532.5	398.0	77.4
Alkaline	Average	409.8	377.7	651.2	92.5
	Min	285.0	20.6	35.9	6.9
	Max	656.0	800.0	1389.0	523.8
NH4OAc-extractable cations					
Acidic	Average	1077.267	166.63	176.17	17.37
	Min	66.00	8.00	17.00	5.00
	Max	3095.00	615.00	575.00	82.00
Alkaline	Average	4277.05	524.05	801.10	89.60
	Min	1951.00	61.00	45.00	11.00
	Max	6360.00	1140.00	1680.00	409.00

Cations (Calcium, Magnesium, Potassium, and Sodium)

The neutral 1.0 *M* NH_4OAc test was used to evaluate Mehlich3 and ABDTPA extraction methods for both acidic and alkaline soils investigated. The average and range of Ca, Mg, K, and Na removed by Mehlich3 and ABDTPA methods, and NH_4OAc test (mg/Kg soil) are given in Table 4.

For both acidic and alkaline soils, the average and range of exchangeable cations, particularly Ca, removed by Mehlich3 were higher than those removed by ABDTPA (Table 4). Meanwhile, amounts of NH_4OAc-extractable cations were slightly lower than those extracted by Mehlich3 method. The combination of acidity (HOAc and HNO_3), and ammonium salts (NH_4F and NH_4NO_3) in Mehlich3 extract appeared to be very effective in removing exchangeable Ca, Mg, K, and Na from soils. Ammonium salts remove exchangeable cations while HOAc and HNO_3 acids can partially dissolve minerals containing these elements such as calcite and dolomite.[14]

Highly significant correlations ($r = 0.747^{**}$ to 0.997^{**}) were obtained between Mg, K, and Na extracted by Mehlich3 or ABDTPA method and NH_4OAc test for both acidic and alkaline soils (Table 5). With respect to Ca, significant correlations were obtained between Mehlich3 method and NH_4OAc test for both acidic ($r = 0.996^{**}$) and alkaline ($r = 0.850^{**}$) soils. On the other hand, ABDTPA method gave significant correlation for acidic soils but failed to show positive relation in alkaline soils.

Precipitation of $CaCO_3$ could explain the failure of ABDTPA extraction method in alkaline soils that usually contain high concentrations of soluble Ca.[17] The fact that some acidic soils might contain high Ca concentration could also explain the relatively low correlation found ($r = 0.570^{**}$) for 30 acidic soils investigated. The effect of $CaCO_3$ precipitation is noticeable for

Table 5. Correlations between Ca, Mg, K, and Na removed by Mehlich3 or ABDTPA extraction methods and NH4OAc test for 30 acidic, and 20 alkaline soils investigated.

Method	Ca	Mg	K	Na
Acidic soils				
Mehlich3	0.996**	0.997**	0.989**	0.747**
ABDTPA	0.570**	0.987**	0.979**	0.866**
Alkaline soils				
Mehlich3	0.850**	0.973**	0.983**	0.996**
ABDTPA	− 0.433*	0.976**	0.956**	0.946**

* and ** indicates 5% and 1% significant level of correlation, respectively.

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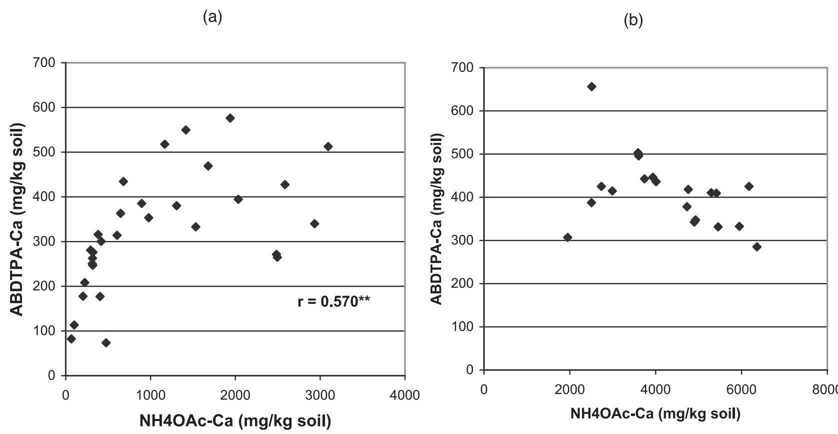

Figure 2. Relationship between ABDTPA-, and NH_4OAc-extractable Ca (mg/Kg soil) for 30 acidic (a), and 20 alkaline (b) soils.

acidic soils with high Ca content (> 1000 mg Ca/Kg soil) (Figure 2a), and for all alkaline soils (Figure 2b).

These results indicated that Mehlich3 method is a good Ca, Mg, K, and Na index for both acidic and alkaline soils while the ABDTPA method could be used successfully for soils of low Ca concentrations. Hanlon and Johnson[15] and Michaelson et al.[18] found significant correlations between exchangeable cations (Ca, Mg, and K) determined by Mehlich3 method and those obtained by NH_4OAc test for Oklahoma, and Alaska soils, respectively. For alkaline soils in Colorado, Soltanpour and Schwab[2] found that ABDTPA method extracted amounts of K similar to those determined by NH_4OAc test.

Heavy Metals (Aluminum, Cadmium, Cobalt, Chromium, Copper, Iron, Manganese, Nickel, Lead, and Zinc)

The average and range of Mehlich3-, ABDTPA-, DTPA-, and 0.1 *M* HCl-extractable Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn for 30 acidic, and 20 alkaline soils investigated are presented in Table 6. In general, the amount of metals removed from soils followed this order: Mehlich3 > ABDTPA > DTPA ≅ 0.1 *M* HCl. Amounts of Al, Fe, and Mn removed from soils (average ranging between 4.14 and 1017 mg/Kg soil) were greater than the other seven metals (Cd, Co, Cr, Cu, Ni, Pb, and Zn). Moderate amounts of Cu, Pb, and Zn (average ranging between 0.11 and 8.94 mg/Kg soil) were

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Table 6. Average and range of metals removed by Mehlich3 and ABDTPA extraction methods, and DTPA, and HCl tests (mg/Kg soil) for 30 acidic, and 20 alkaline soils investigated.

Soils		Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
		mg/kg soil									
Mehlich3-extractable metals											
Acidic	Average	1017.09	0.04	0.27	0.24	2.26	182.76	84.73	0.30	3.42	3.91
	Min	314.14	0.01	0.01	0.01	0.24	49.34	8.25	0.01	0.11	0.44
	Max	1790.56	0.19	1.12	0.34	30.93	294.50	224.02	1.59	27.89	25.81
Alkaline	Average	439.30	0.09	0.72	0.30	3.35	81.48	95.28	0.66	4.07	8.94
	Min	16.75	0.01	0.01	0.07	0.71	23.91	15.58	0.02	0.16	0.70
	Max	1300.33	0.23	1.19	0.45	7.07	281.10	267.84	1.24	7.73	26.51
ABDTPA-extractable metals											
Acidic	Average	29.64	0.11	0.18	0.07	3.19	120.63	55.13	0.32	4.06	4.89
	Min	3.46	0.02	0.05	0.02	0.47	21.62	4.39	0.02	0.62	0.51
	Max	151.67	0.36	0.59	0.28	32.84	341.16	213.41	1.73	37.89	34.52
Alkaline	Average	4.14	0.14	0.18	0.03	4.53	50.90	32.79	0.64	3.33	6.19
	Min	3.25	0.06	0.06	0.01	1.36	7.21	9.44	0.09	0.89	0.82
	Max	15.93	0.30	0.35	0.07	9.48	349.73	68.89	1.51	8.35	16.42

DTPA-TEA-extractable metals											
Acidic	Average	11.41	0.07	0.07	0.08	0.36	14.35	9.71	0.08	0.49	0.64
	Min	0.20	0.01	0.01	0.01	0.01	2.39	0.42	0.01	0.02	0.01
	Max	56.63	0.13	0.16	0.12	2.83	56.95	49.83	0.27	4.46	4.49
Alkaline	Average	0.52	0.08	0.09	0.08	0.48	5.02	4.94	0.12	0.37	0.84
	Min	0.01	0.01	0.01	0.01	0.04	0.65	1.31	0.01	0.01	0.04
	Max	4.31	0.11	0.15	0.11	0.93	29.71	11.76	0.29	0.58	2.62
HCl-extractable metals											
Acidic	Average	67.48	bdl	bdl	bdl	0.31	9.25	10.33	bdl	0.26	0.29
	Min	12.53	bdl	bdl	bdl	0.06	1.59	0.56	bdl	0.04	0.01
	Max	206.38	bdl	bdl	bdl	3.35	37.71	43.30	bdl	2.36	3.34
Alkaline	Average	51.97	bdl	bdl	bdl	0.26	6.04	10.80	bdl	0.11	0.71
	Min	0.03	bdl	bdl	bdl	0.08	0.02	1.77	bdl	0.01	0.01
	Max	148.98	bdl	bdl	bdl	0.99	50.01	74.03	bdl	0.35	3.73

bdl = below detection limit.

determined while those of Cd, Co, Cr, and Ni were extremely low for most soils. Regarding the effect of soil type on metals extraction, amounts of Al, Fe, and Mn removed from acidic soils were generally greater than alkaline soils. The trend was not clear for other metals.

In this study, 0.1 *M* HCl and DTPA tests were used to evaluate both Mehlich3 and ABDTPA extraction methods for acidic, and alkaline soils, respectively. The amounts of Cu, Fe, Mn, Pb, and Zn extracted by the diluted acid test were somewhat close to those removed by DTPA test but it removed more Al than by DTPA test. For all soils, however, the concentration of Cd, Co, and Cr in the diluted acid extract was too low and in most cases were below detection limit of the analytical procedure. Thus, for acidic soils, the diluted acid test was used only to evaluate Al, Fe, Mn, Cu, Ni, Pb, and Zn removed by Mehlich3 and ABDTPA methods.

For acidic soils, the relationship between Mehlich3 or ABDTPA method and HCl test was investigated for Al, Fe, Mn, Cu, Ni, Pb, and Zn. Highly significant correlations ($r = 0.707^{**}$ to 0.994^{**}) were obtained between metals extracted with Mehlich3 method and those removed by the diluted acid test (Table 7). On the other hand, ABDTPA method produced highly significant correlations ($r = 0.519^{**}$ to 0.995^{**}) with all metals except Al, which showed no relation.

In multiple regression analysis, we included soil properties along with the extraction method to improve the relationship particularly for those metals with poor correlations (i.e, Al and Fe). The best two-variable regression models are given in Table 8. The data indicated good improvements in few cases. For example, incorporation of OC with ABDTPA-Al increased the ability to predict variations in the value of HCl-Al from 3.1 to 52.6%. Moreover, including pH with Mehlich3-Fe and ABDTPA-Fe increased the prediction from 50.4 to 57.9% and from 26.9 to 37.3%, respectively.

With respect to Cu, Mn, Pb, and Zn, the best two-variable models which included OC or pH along with Mehlich3-extractable metal (Mehlich3-metal) accounted for 81.9 to 99.0% of variations in the value of 0.1 *M* HCl-extractable metal (HCl-metal). The corresponding prediction levels for ABDTPA extraction method ranged between 80.4 and 99.3%.

Lindsay and Norvell[8] initially introduced the DTPA test to measure the available amounts of Fe, Mn, Cu, and Zn for alkaline and calcareous soils. During the last two decades, however, this test was used successfully to measure heavy metals for both alkaline and acidic soils.[4] Further, as mentioned above, the diluted acid test failed to dissolve measurable amounts of Cd, Co, Cr, and Ni for most soils investigated. Thus, we applied the DTPA test to evaluate Mehlich3 and ABDTPA extraction methods for acidic soils.

For both Mehlich3 and ABDTPA extraction methods, highly significant correlations were obtained for Al, Cu, Fe, Mn, Ni, Pb, and Zn ($r = 0.491^{**}$

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Table 7. Correlations between metals removed by Mehlich3 or ABDTPA extraction method and: i) HCl-extractable metals for 30 acidic soils, and ii) DTPA-extractable metals for 20 alkaline soils.

Method	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
HCl-extractable metals for 30 acidic soils										
Mehlich3	0.835**				0.994**	0.710**	0.707**		0.978**	0.953**
ABDTPA	0.175				0.995**	0.519**	0.866**		0.995**	0.978**
DTPA-extractable metals for 20 alkaline soils										
Mehlich3	0.704**	0.546*	0.033	– 0.144	0.724**	0.880**	0.598**	0.624**	0.606**	0.957**
ABDTPA	0.961**	0.545*	0.132	0.029	0.826**	0.955**	0.872**	0.553**	0.745**	0.979**

* and ** indicate 5% and 1% significant level, respectively.

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Table 8. Best two-variable regression models relating metals removed by Mehlich3 or ABDTPA extraction method and soil properties to 0.1 M HCl test for 30 acidic soils.

Dependent variable	Intercept	Independent variables				R2
		Variable 1	Parameter 1	Variable 2	Parameter 2	
HCl-Al	– 34.896	Mehlich3-Al	0.081	OC	0.951	0.788**
	29.969	ABDTPA-Al	– 0.071	OC	1.907	0.526**
HCl-Cu	0.042	Mehlich3-Cu	0.106	OC	0.002	0.990**
	0.037	ABDTPA-Cu	0.099	OC	– 0.001	0.990**
HCl-Fe	– 26.405	Mehlich3-Fe	0.087	pH	3.423	0.579**
	– 20.051	ABDTPA-Fe	0.049	pH	4.032	0.373**
HCl-Mn	– 4.169	Mehlich3-Mn	0.090	OC	0.331	0.819**
	– 26.017	ABDTPA-Mn	0.207	pH	4.299	0.804**
HCl-Pb	– 0.084	Mehlich3-Pb	0.080	OC	0.003	0.975**
	0.040	ABDTPA-Pb	0.063	OC	– 0.002	0.993**
HCl-Zn	– 0.378	Mehlich3-Zn	0.124	OC	0.009	0.945**
	– 0.615	ABDTPA-Zn	0.106	pH	0.066	0.960**

* and ** indicate 5% and 1% significant level, respectively.

to 0.986**) while no relation was found for Cd, Co, and Cr. The extremely small amounts of Cd, Co, and Cr detected for most soils investigated may explain the absence of any significant correlation. The correlation data between metals extracted by Mehlich3 or ABDTPA method and DTPA test for acidic soils are not given in this report.

For acidic soils, incorporation of soil properties along with Mehlich3-metal or ABDTPA-metal in a multiple regression model improved the relationship with DTPA test. The best two-variable regression models are given in Table 9. When OC or clay was incorporated along with Mehlich3-metal, the two-variable models could account for 40.7 to 96.2% of variations in the value of DTPA-metal. For ABDTPA extraction method, the corresponding values ranged between 58.1 and 98.0%. These data suggested that either Mehlich3 or ABDTPA extraction method could be used for Al, Cu, Fe, Mn, Ni, Pb, and Zn extraction in acidic soils. With respect to Cd, Co, and Cr, future study on soils having measurable amounts of these metals might allow successful evaluation.

Other investigators reported improvements in predicting available metals when soil properties were included with DTPA in multiple regression models. Haq et al.,[19] in their study on Canadian soils, found that inclusion of soil pH with DTPA in multiple regression models could account for 80–81% of variations in the value of plant available Zn, Cd, and Ni. Korcak and Fanning[20] also reported successful use of DTPA and pH in predicting plant available Cd, Cu, Ni, and Zn in Coastal Plain of the USA.

For the alkaline soils, the DTPA test was used to evaluate Mehlich3 and ABDTPA extraction methods. The data (Table 7) show highly significant correlations ($r = 0.553^{**}$ to 0.979^{**}) between amounts of Al, Cu, Fe, Mn, Ni, Pb, and Zn extracted by Mehlich3 or ABDTPA method and those removed by DTPA test. The relationship was significant at the 5% level for extractable Cd. On the other hand, no relation was obtained for both Co, and Cr due to the extremely small amounts of Co and Cr extracted from the soils. Soltanpour[17] reported high degree of correlations between ABDTPA-, and DTPA-extractable Cu, Mn, and Zn for alkaline soils in Colorado.

In general, incorporation of soil properties along with Mehlich3- or ABDTPA-metal improved the relationship with DTPA-metal. For 20 alkaline soils, the best two-variable regression models relating metals extracted with Mehlich3 or ABDTPA method and soil properties to DTPA-extractable metals are given in Table 9. When clay or pH was added to Mehlich3-metal or ABDTPA-metal, the model could account for most of variations in the value of the respective DTPA-metal.

Similar to the assessment made above for acidic soils, either Mehlich3 or ABDTPA extraction method appeared to be an appropriate measurement

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Table 9. Best two-variable regression models relating metals removed by Mehlich3 or ABDTPA extraction method and soil properties to DTPA test for 30 acidic, and 20 alkaline soils investigated.

Dependent variable	Intercept	Independent variables: Variable 1	Parameter 1	Variable 2	Parameter 2	R2
Thirty acidic soils						
DTPA-Al	− 0.689	Mehlich3-Al	0.006	OC	0.286	0.407**
	0.407	ABDTPA-Al	0.190	OC	0.259	0.656**
DTPA-Cu	0.048	Mehlich3-Cu	0.092	clay	0.010	0.944**
	0.035	ABDTPA-Cu	0.086	clay	0.005	0.980**
DTPA-Fe	− 6.258	Mehlich3-Fe	0.072	OC	0.363	0.547**
	− 3.885	ABDTPA-Fe	0.136	clay	0.166	0.881**
DTPA-Mn	− 3.558	Mehlich3-Mn	0.092	OC	0.265	0.781**
	− 1.899	ABDTPA-Mn	0.186	clay	0.120	0.939**
DTPA-Ni	0.055	Mehlich3-Ni	0.105	OC	− 0.001	0.575**
	0.061	ABDTPA-Ni	0.095	OC	− 0.001	0.581**
DTPA-Pb	− 0.310	Mehlich3-Pb	0.146	OC	0.014	0.916**
	− 0.082	ABDTPA-Pb	0.120	OC	0.004	0.974**
DTPA-Zn	− 0.261	Mehlich3-Zn	0.156	OC	0.014	0.962**
	− 0.092	ABDTPA-Zn	0.136	clay	0.006	0.976**

Twenty alkaline soils						
DTPA-Al	0.535	Mehlich3-Al	0.002	clay	− 0.036	0.758**
	− 0.411	ABDTPA-Al	0.306	clay	− 0.012	0.949**
DTPA-Cu	1.276	Mehlich3-Cu	0.104	pH	− 0.149	0.590**
	1.225	ABDTPA-Cu	0.082	pH	− 0.145	0.745**
DTPA-Fe	− 4.233	Mehlich3-Fe	0.087	clay	0.080	0.797**
	− 1.880	ABDTPA-Fe	0.087	clay	0.090	0.941**
DTPA-Mn	28.512	Mehlich3-Mn	0.015	pH	− 3.237	0.468**
	− 0.504	ABDTPA-Mn	0.129	clay	0.045	0.828**
DTPA-Ni	0.083	Mehlich3-Ni	0.187	clay	− 0.003	0.700**
	0.094	ABDTPA-Ni	0.142	clay	− 0.002	0.500**
DTPA-Pb	0.079	Mehlich3-Pb	0.039	clay	0.005	0.552**
	0.057	ABDTPA-Pb	0.057	clay	0.004	0.716**
DTPA-Zn	1.351	Mehlich3-Zn	0.091	pH	− 0.171	0.924**
	2.091	ABDTPA-Zn	0.153	pH	− 0.284	0.978**

* and ** indicate 5% and 1% significant level, respectively.

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for Al, Cd, Cu, Fe, Mn, Ni, Pb, and Zn in the 20 alkaline soils investigated. The fact that these soils have trace amounts of some metals (i.e., Co and Cr) hindered their evaluation.

CONCLUSIONS

Work related to nutrient best management practices, precision farming, and sustainable agriculture programs, along with the growing concern about agricultural land as a non-point source of contamination have emphasized the great need for a multi-element soil test. A multi-element extraction that works as an agronomic and environmental soil test is also desirable for its economical and scientific benefits. In the light of the data obtained, it was concluded that Mehlich3 extraction can be recommended for simultaneous measurement of available P, cations (Ca, Mg, K, and Na), and soluble metals (Al, Cd, Cu, Fe, Mn, Ni, Pb, and Zn) for all soils. For alkaline and calcareous soils, however, ABDTPA extraction can be used for measurement of all these elements except for Ca. Further research on agricultural soils having measurable contents of Co, Cr, As, and Se would be required to investigate the possibility of adding more metals.

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